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<b>(21) International Application Number:</b> PCT/EP97/02978 <b>(22) International Filing Date:</b> 4 June 1997 (04.06.97)  <b>(30) Priority Data:</b> 08/659,479                      5 June 1996 (05.06.96) <b>US</b>  <b>(71) Applicant:</b> SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).  <b>(72) Inventor:</b> LOCKEMEYER, John, Robert; 3403 Stoney Mist Drive, Sugar Land, TX 77479 (US).		<b>(81) Designated States:</b> JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> EPOXIDATION CATALYST AND PROCESS  <b>(57) Abstract</b>  This invention relates to an epoxidation catalyst which contains silver, one or more alkali metal promoters optionally rhenium and optionally rhenium co-promoter supported on an alpha alumina carrier in which a fired carrier body is impregnated with a source of titania in a liquid medium that upon heating yields titania and is then calcined to generate titania uniformly dispersed in the carrier in an amount of up to 10 percent by weight, basis the total weight of the carrier.		

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- 1 -

## EPOXIDATION CATALYST AND PROCESS

5 The invention relates to silver-containing catalysts suitable for the epoxidation of olefins having no allylic hydrogen, in particular for the preparation of ethylene oxide and to the use of the catalysts for the preparation of ethylene oxide. The catalysts are prepared using carriers based on ceramic components.

10 Catalysts for the production of ethylene oxide from ethylene and molecular oxygen are generally supported silver catalysts. Such catalysts are typically promoted with alkali metals. The use of small amounts of the alkali metals potassium, rubidium and cesium were noted as useful promoters in supported silver catalysts in U.S. Patent No. 3,962,136, issued June 8, 1976, and U.S. Patent No. 4,010,115, issued March 1, 1977. The use of other co-promoters, such as rhenium, or rhenium along with sulphur, molybdenum, tungsten and chromium is disclosed in U.S. Patent No. 4,766,105, issued August 23, 1988, and U.S. Patent No. 4,808,738, issued February 28, 1989. U.S. Patent No. 4,908,343, issued March 13, 1990, discloses a supported silver catalyst containing a mixture of a cesium salt and one or more alkali metal and alkaline earth metal salts.

25 The use of ceramic based catalyst carriers and specifically alpha alumina based catalyst carriers has been previously described in a number of patents such as, for example, U.S. Patent No. 5,100,859, issued March 31, 1992, U.S. Patent No. 5,055,442, issued October 8, 1991, U.S. Patent No. 5,037,794, issued August 6, 1991, and U.S. Patent No. 4,874,739, issued October 17, 1989.

- 2 -

A catalyst support or carrier needs to possess, in combination, at least a minimum surface area on which the catalytic component may be deposited, high water absorption and crush strength. The problem is that usually an increase in one can mean a reduction in another property. Thus, high crush strength may mean low porosity. Often the balance is achieved by trial and error making the catalyst carrier art even more unpredictable than other chemical process art.

Carriers based on alpha alumina have an excellent balance of crush strength, abrasion resistance, porosity and catalytic performance that makes them ideal for a range of catalytic applications. It has been found that the physical properties can be improved by incorporating a titania component into the mixture fired to produce the carrier. While such titania modification has been found to greatly improve physical properties such as crush strength and abrasion resistance, it has been found that it also tends to affect the densification of the carrier structure and this can lead to unacceptable properties. This problem increases with increasing concentration of added titania.

There is therefore a need to provide for the incorporation of the highly beneficial titania component into the carrier without causing such densification such that the catalysts prepared therefrom have acceptable physical properties and performance characteristics. The catalysts of the present invention have excellent physical properties and catalytic performance that make them ideal for a wide range of catalytic applications.

This invention relates to a catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular for the vapour phase production of ethylene oxide from ethylene and oxygen, comprising a catalytically effective amount of silver and a promoting

- 3 -

amount of alkali metal, optionally a promoting amount of rhenium and optionally a rhenium co-promoter, deposited on a carrier which carrier is prepared by a process comprising:

- 5 a) forming a mixture of ceramic components comprising at least one alumina component, ceramic bond, and a liquid medium;
- b) shaping the mixture into carrier bodies;
- c) drying and firing the bodies at a temperature of from  
10 1200 °C to 1500 °C to form porous carrier bodies;
- d) impregnating the porous carrier bodies with a titania generator in a liquid medium; and then
- e) calcining the impregnated bodies at a temperature sufficient to remove volatiles and generate titania.

15 It has been found that catalysts having this alpha alumina based carrier have improved initial activity and/or selectivity.

The present invention provides an advance over the disclosure in U.S. Patent No. 5,380,697, issued  
20 January 10, 1995, in that it teaches the advantages of a catalyst in which addition of the titania component is by impregnation of the fired porous carrier prior to deposition of a catalyst on the carrier.

In the discussion that follows the invention will be  
25 discussed in terms of added "titania" because, after the firing operation, it is assumed for the purposes of this specification that the titanium remaining in the carrier will be in the form of an oxide.

Since titania is not soluble in water, it must be  
30 carried in to the pores of the fired porous carrier in solution or sol form. It should be understood therefore that any suitable soluble titanium compound can be used provided that it decomposes to the oxide and leaves no residue or evolves no components that could interfere  
35 with the activity or performance of the catalyst

- 4 -

deposited on the carrier. Thus, ammonium titanyl oxalate, titanium (IV) bis(ammonium lactato) dihydroxide, as well as any other similar organic compounds are suitable. In addition, titania sols or slurries of heat-decomposable titanium compounds are usable providing they are fluid enough to penetrate the pores of the carrier. It is also possible to use a titanium alkoxide or other organometallic compound in a suitable liquid vehicle.

As used in this specification, the term "titania generator" is understood to embrace all such suitable soluble titanium compounds, slurries and sols that, under the conditions under which the carrier is produced, form titania.

Generally, the use of a titanium salt as the titania generator is preferred and the oxalate or dihydroxy bis-lactate are the most preferred titanium salts because they are very soluble and because they decompose at relatively low temperatures of from 200 °C to 320 °C. Upon decomposition, an amorphous titania phase is formed which generally has too high a surface area for optimum results. It is preferred to calcine the impregnated carrier at a temperature at or above 450 °C to 500 °C at which the anatase form is generated. Heating at higher temperatures above 773 °C generates the rutile form. Neither of these consequences is disastrous, especially if a larger amount of titania towards the upper end of the preferred range is used, however it should be noted that prolonged exposure to higher temperatures can lead to the titania sintering and forming larger crystals which, in general, is not desirable. It is therefore desirable to calcine the impregnated carrier at a temperature in the range of from 400 °C to 1400 °C, preferably from 400 °C to 700 °C, and more preferably in the range of from 500 °C to 600 °C, and for a time in the

- 5 -

range of from 15 minutes to 120 minutes and preferably in the range of from 30 minutes to 60 minutes.

It is advantageous to add the titania generator in an amount which represents from 0.05 percent to 10 percent, and more preferably from 0.1 percent to 2.0 percent of the weight of the fired carrier, (calculated as  $\text{TiO}_2$ ). Generally speaking, little selectivity advantage is seen as a result of incorporating more than 0.5 percent of titania. Impregnation is preferably done by saturating the carrier particles with a solution of a titania generator which is then decomposed to titania when the carrier particles are calcined.

The calcination of the impregnated carrier is carried out under conditions adapted to generate titania.

Certain forms of alumina and bond material may also contain titania as impurities or components. The contribution of such forms of titania are not included in the amounts specified above.

The carrier is heated at a temperature that is high enough to sinter the alumina particles and produce a structure with physical properties adequate to withstand the environment in which it is expected to operate. In practice, temperatures in the range of from 1200 °C to 1500 °C and particularly in the range of from 1300 °C to 1500 °C are used to perform this sintering. It should be understood that lower temperatures usually require longer times to achieve the same degree of sintering as higher temperatures. Sintering may be carried out either before or after the impregnation or if desired, at the time the catalyst components are placed on the carrier. Preferably, sintering is carried out prior to impregnation.

The preferred catalyst carrier of the invention may comprise a number of alpha alumina components chosen to contribute to the desired physical properties, including porosity, pore volume, crush strength and the like.

- 6 -

Often, a combination of two different alpha aluminas is preferred, one component having larger particles mixed with a second component having smaller particles, in weight ratios of from 10:90 to 90:10. The objective of this is to end up with a surface area, (in this document a reference to "surface area" is understood to mean the BET surface area measured using nitrogen or krypton as the adsorbed gas), in the finished product of from 0.4 square meters/gram ( $\text{m}^2/\text{g}$ ) to  $5 \text{ m}^2/\text{g}$ . The surface area in the finished carrier is somewhat less than for the free alumina particles. Thus, a convenient mixture may comprise for example, two types of alpha alumina particles, the first having a surface area of  $1 \text{ m}^2/\text{g}$  and the second having a surface area of  $3 \text{ m}^2/\text{g}$  to  $5 \text{ m}^2/\text{g}$ .

Part of the alpha alumina may be formed in situ from a precursor which is preferably boehmite. Good results are also obtained if the precursor comprises a mixture of boehmite with an aluminium trihydrate such as gibbsite or bayerite. Where such a mixture is used it is often preferred to use a weight ratio of the monohydrate, (boehmite), to trihydrate of from 1:10 to 1:3 and more preferably from 1:8 to 1:4. It is often preferred that, when a sol is formed from the precursor by addition of water, a submicrometer particle sized seed material is also added. This has the effect of reducing the temperature at which the transition to alpha alumina occurs and reduces the crystal size of the alpha alumina produced upon transformation.

The seed used can be any material that is effective to produce nucleation sites in the precursor so as to reduce the transition temperature at which a transition alumina converts to alpha alumina. Seeds that accomplish this goal typically have the same crystal lattice type as alpha alumina itself and lattice dimensions that do not differ significantly from those of alpha alumina.

- 7 -

Clearly, the most convenient seed is alpha alumina itself and sub-micrometer sized particles of alpha alumina are the preferred seed. It is, however, possible to use other seeds such as alpha ferric oxide and chromium oxide.

Alpha alumina formed from the preferred seeded precursor when the extruded mixture is fired generally has a much finer crystal size than the alpha alumina particles with which the seeded precursor is mixed unless, during firing, it is maintained at a high temperature for a prolonged period. As produced, the seeded sol-gel material has a sub-micrometer crystal structure but if it is held at temperatures over about 1400 °C for extended periods, crystal growth begins and the size differentiation may become less apparent.

The carrier of the invention preferably has a porosity of at least 50 percent and more desirably from 60 percent to 75 percent. The porosity is related to the surface area which is preferably from 0.4 m<sup>2</sup>/g to 5 m<sup>2</sup>/g, and more preferably from 0.6 m<sup>2</sup>/g to 1.2 m<sup>2</sup>/g. The porosity may be obtained by addition of organic burnout material such as ground walnut shells or solid particles of a combustible hydrocarbon. Porosity may also be obtained without the use of burnout material by choice of particle sizes of the ceramic components sintered together to form the carrier.

It is usually preferred to add a ceramic bond material to the mixture from which the carrier is to be made to give added strength to the fired carrier. Conventional ceramic bond materials can be used and after firing these typically comprise components, (expressed as the oxides), such as silica, alumina, alkaline earth metal oxides, alkali metal oxides, iron oxide and titanium oxide, with the first two being the dominant components. It is found that bond materials containing

- 8 -

significant amounts of alkali metals, that is up to about 5 percent by weight and more preferably from 2 percent by weight to 4 percent by weight are particularly suitable. Particularly suitable bond materials include calcium  
5 silicate and magnesium silicate either added as such or formed in situ.

The carriers described above are particularly suited for preparing epoxidation catalysts which have improved physical properties with respect to crush strength and  
10 abrasion resistance.

The catalysts of the present invention comprise a catalytically effective amount of silver and a promoting amount of alkali metal(s) deposited on a carrier prepared as described above. Other promoters in promoting amounts  
15 may be optionally present such as rare earths, magnesium, rhenium and rhenium co-promoters selected from sulphur, chromium, molybdenum, tungsten, phosphorus, boron and mixtures thereof.

In general, the catalysts of the present invention are prepared by impregnating the carrier with silver ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause deposition on the support of from 1 to 40, preferably from 1 to 30 percent by weight, basis the weight of the total catalyst, of  
20 silver. The impregnated support is then separated from the solution and the deposited silver compound is reduced to metallic silver. Also deposited on the support either prior to, coincidentally with, or subsequent to the deposition of the silver will be suitable ions, or  
25 compound(s) and/or salt(s) of alkali metal dissolved in a suitable solvent. Also deposited on the carrier coincidentally with the deposition of the silver and/or alkali metal will be suitable optional promoter compound(s), complex(es) and/or salt(s) dissolved in an  
30 appropriate solvent.  
35

- 9 -

The catalysts of the present invention are prepared by a technique in which the alkali metal promoter as well as any additional promoters in the form of soluble salts and/or compounds are deposited on the catalyst and/or support prior to, simultaneously with, or subsequent to the deposition of the silver and each other. The preferred method is to deposit silver, alkali metal and any additional promoters simultaneously on the support, that is, in a single impregnation step, although it is believed that the individual or concurrent deposition of the alkali metal prior to and/or subsequent to the deposition of the silver would also produce suitable catalysts.

Promoting amounts of alkali metal or mixtures of alkali metal are deposited on a porous support using a suitable solution. Although alkali metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds of alkali metals dissolved in a suitable solvent for impregnation purposes. The carrier is impregnated with a solution of alkali metal promoter ions, salt(s) and/or compound(s) before, during or after impregnation of the silver ions or salt(s), complex(es), and/or compound(s) has taken place. An alkali metal promoter may even be deposited on the carrier after reduction to metallic silver has taken place. The promoting amount of alkali metal utilized will depend on several variables, such as, for example, the surface area and pore structure and surface chemical properties of the carrier used, the silver content of the catalyst and the particular ions used in conjunction with the alkali metal cation, optional co-promoters. The amount of alkali metal promoter deposited upon the support or present on the catalyst generally lies between 10 and 3000, preferably between 15 and 2000, more preferably between 20 and 1500 and most preferably, the

- 10 -

amount ranges between 50 and 1000 parts per million by weight of the total catalyst. The alkali metal promoters are present on the catalysts in the form of cations (ions) or compounds of complexes or surface compounds or surface complexes rather than as the extremely active free alkali metals, although for convenience purposes in this specification and claims they are referred to as "alkali metal" or "alkali metal promoters" even though they are not present on the catalyst as metallic elements. Without intending to limit the scope of the invention, it is believed that the alkali metal compounds are oxidic compounds.

In a preferred embodiment, at least a major proportion (greater than 50% wt.) of the alkali metals are selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof. As used herein, the term "alkali metal" and cognates thereof refers to the alkali metals selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and mixtures thereof. As used herein, the term "mixtures of alkali metals" or cognates of these terms refers to the use of two or more of the alkali metals, as appropriate, to provide a promoting effect. Non-limiting examples include cesium plus rubidium, cesium plus potassium, cesium plus sodium, cesium plus lithium, cesium plus rubidium plus sodium, cesium plus potassium plus sodium, cesium plus lithium plus sodium, cesium plus rubidium plus potassium plus sodium, cesium plus rubidium plus potassium plus lithium, cesium plus potassium plus lithium and the like. A preferred alkali metal promoter is cesium.

Non-limiting examples of other promoters include rhenium, sulphate, molybdate, tungstate and chromate (see U.S. Patent no. 4,766,105, issued August 23, 1988), as well as phosphate and borate; sulphate anion, fluoride

- 11 -

anion, oxyanions of Groups 3b to 6b (see U.S. Patent No. 5,102,848, issued April 7, 1992); (i) oxyanions of an element selected from Groups 3 through 7b and (ii) alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups 3a to 7a and 3b through 7b (see U.S. Patent No. 4,908,343, issued March 13, 1990).

One method of preparing the silver containing catalyst can be found in U.S. Patent 3,702,259, issued November 7, 1972. Other methods for preparing the silver-containing catalysts which in addition contain higher alkali metal promoters can be found in U.S.

Patent 4,010,115, issued March 1, 1977; and U.S.

Patent 4,356,312, issued October 26, 1982; U.S.

Patent 3,962,136, issued June 8, 1976 and U.S.

Patent 4,012,425, issued March 15, 1977. Methods for preparing silver-containing catalysts containing higher alkali metal and rhenium promoters can be found in U.S.

Patent No. 4,761,394, issued August 2, 1988, and methods for silver-containing catalysts containing higher alkali metal and rhenium promoters and rhenium co-promoters can be found in U.S. Patent No. 4,766,105, issued August 2, 1988. Methods for preparing silver-containing catalysts with a variety of different promoters are found in U.S.

patents 4,908,343, issued March 13, 1990 and 5,057,481, issued October 15, 1991.

A particularly preferred process of impregnating the carrier consists of impregnating the carrier with an aqueous solution containing a silver salt of a carboxylic acid, an organic amine and a salt of cesium and a salt of an additional alkali dissolved therein. Silver oxalate is a preferred salt. The impregnated carriers are heated to a temperature between 50 °C and 600 °C, preferably between 75 °C and 400 °C to evaporate the liquid and produce a metallic silver.

- 12 -

In general terms, the impregnation process comprises impregnating the support with one or more solutions comprising silver, alkali metal and optionally, other promoters. The concentration of the silver (expressed as the metal) in the silver-containing solution will range from 1 g/l up to the solubility limit when a single impregnation is utilized. The concentration of the alkali metal (expressed as the metal) will range from  $1 \times 10^{-3}$  g/l up to 12 g/l and preferably, from  $10 \times 10^{-3}$  g/l to 12 g/l when a single impregnation step is utilized. Concentrations selected within the above noted ranges will depend upon the pore volume of the catalyst, the final amount desired in the final catalyst and whether the impregnation is single or multiple. Appropriate concentrations can be readily determined by routine experimentation.

It is observed that independent of the form in which the silver is present in the solution before precipitation on the carrier, the term "reduction to metallic silver" is used, while in the meantime often decomposition by heating occurs. We prefer to use the term "reduction", since  $\text{Ag}^+$  ion is converted into a metallic Ag atom. Reduction times may generally vary from 0.5 minute to 8 hours, depending on the circumstances.

In commercial operation, ethylene and oxygen are converted to ethylene oxide in an ethylene oxide reactor which comprises a large fixed tube heat exchanger containing several thousand tubes filled with catalysts. A coolant is used on the shell side of the reactor to remove the heat of reaction. Coolant temperatures are frequently utilized as an indication of catalyst activity, with high coolant temperatures corresponding to lower catalyst activities.

- 13 -

In the reaction of ethylene oxide with oxygen to produce ethylene oxide, the ethylene is typically present in at least a double amount (on a molar basis) compared with oxygen, but the amount of ethylene employed is generally much higher. The conversion is therefore conveniently calculated according to the mole percentage of oxygen which has been consumed in the reaction to form ethylene oxide and any oxygenated by-products. The oxygen conversion is dependent on the reaction temperature, and the reaction temperature is a measure of the activity of the catalyst employed. The value  $T_{1.5}$  indicates the temperature expressed in °C at 1.5 percent ethylene oxide production, and the value  $T$  is expressed in °C. The selectivity (to ethylene oxide) indicates the molar amount of ethylene oxide in the reaction product compared with the total molar amount of ethylene converted. In this specification, the selectivity is indicated as  $S_{1.5}$ , which means the selectivity at 1.5 percent ethylene oxide production.

The conditions for carrying out such an oxidation reaction in the presence of the silver catalysts according to the present invention broadly comprise those already described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, diluent materials such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, to the presence of moderating agents to control the catalytic action, for example, 1-2-dichloroethane, vinyl chloride, ethyl chloride or chlorinated polyphenyl compounds, to the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and to any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to 3500 kPa

- 14 -

are generally employed. Higher pressures, however, are not excluded. Molecular oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist essentially or relatively pure oxygen, a concentrated oxygen stream comprising oxygen in major amount with lesser amounts of one or more diluents, such as nitrogen and argon, or another oxygen-containing stream, such as air. It is therefore evident that the use of the present silver catalysts in ethylene oxide reactions is in no way limited to the use of specific conditions among those which are known to be effective. For purposes of illustration only, the following table shows the range of conditions that are often used in current commercial ethylene oxide reactor units and which are also suitable for the instant process.

TABLE I

*GHSV	1500-10,000
Inlet Pressure	1034-2756 kPa
<u>Inlet Feed</u>	
Ethylene	1-40%
O <sub>2</sub>	3-12%
Ethane	0-3%
Chlorohydrocarbon moderator	0.3-50 ppmv total
Argon and/or methane and/or nitrogen diluent	Balance
Coolant temperature	180-315 °C
Catalyst temperature	180-325 °C
O <sub>2</sub> conversion level	10-60%
EO Production (Work Rate)	26-325 kg/l of catalyst/hr

\*Units of volume of gas at standard temperature and pressure passing over unit of volume of packed catalyst per hour.

- 15 -

5 In a preferred application of the silver catalysts according to the invention, ethylene oxide is produced when an oxygen-containing gas is contacted with ethylene in the presence of the present catalysts at a temperature in the range of from 180 °C to 330 °C, and preferably a temperature in the range of from 200 °C to 325 °C.

10 While the catalysts of the present invention are preferably used to convert ethylene and oxygen to ethylene oxide, other olefins having no allylic hydrogens can be oxidized using the silver catalysts of the present invention to produce a high selectivity of epoxide derivatives thereof by contacting the olefin feed with an oxygen-containing gas in the presence of an organic halide and the silver catalyst described above under  
15 defined oxidation conditions. The catalysts of the present invention may also be utilized to oxidize mixtures of olefins.

20 The process for the selective epoxidation of olefins having at least three carbon atoms comprises contacting the feed olefin with a sufficient quantity of an oxygen-containing gas so as to maintain the molar ratio of olefin to oxygen in the range of 0.01 up to 20, in the presence of an organic halide and a silver catalyst at a reaction pressure in the range of 10 up to 10.000 kPa  
25 and a temperature in the range of 75° up to 325 °C for a reaction time sufficient to obtain olefin conversions per pass in the range of 0.1 up to 75 mole percent.

30 The process is carried out in the presence of sufficient quantities of an oxygen-containing gas to provide a molar ratio of olefin to oxygen in the range of 0.01 up to 20, and in the presence of 0.1 up to 1000 parts per million (by volume of total feed) of organic halide. Preferred quantities of organic halide for use in the practice of the present invention fall within the

- 16 -

range of 1 up to 100 parts per million, by volume of total feed.

Prior to use for oxidizing olefins having at least three carbon atoms, the silver catalysts (either before  
5 or after further treatment with promoter), are optionally calcined in an oxygen-containing atmosphere (air or oxygen-supplemented helium) at 350 °C for 4 hours. Following calcination, the silver catalysts are typically subjected to an activation treatment at a temperature in  
10 the range of 300°-350 °C in an atmosphere initially containing 2-5% hydrogen in an inert carrier such as helium or nitrogen. The hydrogen content of the activating atmosphere is gradually increased up to a final hydrogen concentration of 20-25% at a controlled  
15 rate so that the activation temperature does not exceed 350 °C. After the temperature is maintained for about 1 hour at a hydrogen concentration in the range of 20-25%, catalyst is ready for use.

More detailed descriptions of the silver catalysts and their use in oxidizing olefins having at least three  
20 carbon atoms are found in U.S. Patent Nos. 4,897,498, issued January 30, 1990 and 5,081,096, issued January 14, 1992.

The invention will be illustrated by the following  
25 examples.

#### Examples

##### Carrier Preparation

###### Carrier A:

The ceramic components are mixed with a burn-out  
30 material (walnut shell flour), and boric acid for about a minute. Water and an alpha alumina seed component are then added, the water being added in an amount that is necessary to make the mixture extrudable. Generally this is about 30% by weight of the total solids present. The  
35 mixture is mixed for 4.5 minutes and then 5% by weight,

- 17 -

based on the weight of the ceramic components, of  
vaseline is added as an extrusion aid. The mixture is  
then mixed for a further 3.5 minutes before being  
extruded in the form of hollow cylinders and dried to  
remove essentially all bound water. These were then  
fired in a tunnel kiln with a maximum temperature of  
1460-1490 °C for 5 hours.

The fired carrier was divided into two portions and  
one portion was impregnated with a titania-generating  
material in an amount sufficient to give a final titanium  
content in the dried and finished carrier of 0.05 percent  
by weight.

The impregnation was carried out by weighing out a  
solution of titanium(IV) bis(ammonium lactato) dihydro-  
xide, commercially available as "TYZOR LA", in an amount  
necessary to give a final level titanium content in the  
final carrier of 0.05 percent by weight. The total  
volume of solution used was equivalent to the pore volume  
of the carrier.

The carrier was impregnated by slow addition to the  
carrier in pellet form with agitation. When addition was  
complete, the impregnated carrier was allowed to stand  
for thirty minutes and then dried overnight at 120 °C.  
It was then calcined at 500 °C for six hours. The  
carrier is described in terms of its formulation in  
Table 1 and in terms of its physical properties in  
Table 2.

Carrier B:

Carrier B was prepared in a manner similar to  
Carrier A except that the impregnation was done with  
deionized water containing no titania-generating  
material. The carrier is described in terms of its  
formulation in Table 1 and in terms of its physical  
properties in Table 2.

Carrier C:

- 18 -

Carrier C was prepared in a manner similar to Carrier A except that the carrier contains no alpha alumina component generated by a sol-gel process, and no seed component, i.e., Alpha Alumina #5, was added to the carrier formulation. The carrier is described in terms of its formulation in Table 1 and in terms of its physical properties in Table 2.

Carrier D:

Carrier D was prepared in a manner similar to Carrier C except that the impregnation was done with deionized water containing no titania-generating material. The carrier is described in terms of its formulation in Table 1 and in terms of its physical properties in Table 2.

- 19 -

TABLE 1  
CARRIER COMPOSITIONS

	Carrier A, %wt.	Carrier B, %wt.	Carrier C, %wt.	Carrier D, %wt.
Alpha Alumina #1 1,2	46.7	46.7	None	None
Alpha Alumina #2 1,3	27.4	27.4	None	None
Alpha Alumina #3 (Seed) 1,4	2.2	2.2	None	None
Alpha Alumina #4 1,5	None	None	74.5	74.5
Alpha Alumina #5 1,6	None	None	24.5	24.5
Titanium 1	0.05	None	0.05	None
Gibbsite 1,7	18.3	18.7	None	None
Boehmite 1,8	4.1	4.5	None	None
Ceramic Bond 1,9,10	1.3	1.3	1.0	1.0
Organic Burnout 11	20.0	11.0	25.0	25.0
Vaseline <sup>11</sup>	5.0	5.0	5.0	5.0
Boric Acid <sup>11</sup>	0.15	0.15	0.1	0.1
Water (to make extrudable) <sup>12</sup>	~30	~30	~30	~30

1 Indicates "ceramic components" and percentages given are based on 100% of the ceramic components.

2 "Alpha Alumina #1" is an alpha alumina that had a median particle size of about 3 to about 3.4 microns, a BET surface area of about 0.9 to 1.4 m<sup>2</sup>/g, a crystallite size of 1.6 to 2.2 micrometer and a soda content of 0.02% to 0.06%.

3 "Alpha Alumina #2" is an alpha alumina with a median particle size of 4.0 to 8.0 micrometer, a surface

- 20 -

area of 3.0 to 5.0 m<sup>2</sup>/g, a crystallite size of from 0.4 to 0.8 micrometer and a soda content of 0.1% to 0.3%.

4 "Alpha Alumina #3" is an alpha alumina that was used  
5 as the seed for the gibbsite and boehmite precursors  
of alpha alumina. Its median particle size was less  
than 0.1 micrometer.

5 "Alpha Alumina #4" is an alpha alumina that had a  
median particle size of 3.0 to 4.0 microns, a  
10 crystallite size of 3.0 to 3.2 micrometer and a soda  
content of 0.02% to 0.03%.

6 "Alpha Alumina #5" is an alpha alumina with a median  
particle size of 2.5 to 3.7 microns, a crystallite  
size of from 2.0 to 2.5 micrometer and a soda content  
15 of 0.08% to 0.10%.

7 The gibbsite had a median particle size of from 4.0  
to 20 micrometer.

8 The boehmite was dispersible as a sol.

9 The ceramic bond for carriers A and B contained  
20 components, expressed as the oxides, in the following  
approximate proportions: 61.3% wt. SiO<sub>2</sub>, 28.6% wt.  
Al<sub>2</sub>O<sub>3</sub>, 0.85% wt. Fe<sub>2</sub>O<sub>3</sub>, 0.68% wt. TiO<sub>2</sub>, 2.92% wt.  
CaO, 1.79% wt. MgO, 1.15% wt. Na<sub>2</sub>O and 2.67% wt. K<sub>2</sub>O.

10 The ceramic bond for carriers C and D contained  
25 components, expressed as the oxides, in the following  
approximate proportions: 58.76% wt. SiO<sub>2</sub>, 36.55% wt.  
Al<sub>2</sub>O<sub>3</sub>, 1.22% wt. Fe<sub>2</sub>O<sub>3</sub>, 1.51% wt. TiO<sub>2</sub>, 0.90% wt.  
CaO, 0.26% wt. MgO, 0.11% wt. Na<sub>2</sub>O, and 0.57% wt.  
K<sub>2</sub>O.

30 11 Percentages are based on the total weight of the  
ceramic components.

12 Percentages are based on total weight of solids.

- 21 -

TABLE 2  
CARRIER PROPERTIES

PROPERTY	Carrier A	Carrier B	Carrier C	Carrier D
Fired Temp. °C	500	500	500	500
Surface Area <sup>1</sup> (m <sup>2</sup> /g)	1.06	1.06	0.5	0.5
Pack. Den. <sup>2</sup> (kg/litre <sup>3</sup> )	0.713	0.713	0.738	0.730
Water Ab- sorp. <sup>3</sup> (%)	45.9	45.9	43.9	43.9

<sup>1</sup> "Surface Area" is the BET surface area measured using nitrogen or krypton as the adsorbate.

<sup>2</sup> "Packing Density" is the settled packing density as measured by ASTM D-4699-87, modified by the use of cylinder with an inside diameter of 95 mm and a length of 457 mm, or an equivalent.

<sup>3</sup> "Water Absorption" is a measure of the increase in weight of the carrier after being immersed in water and weighed.

#### 10 Catalyst Preparation

The following illustrative embodiment describes preparative techniques for making the catalysts of the instant invention (Catalysts A and C) and the comparative catalysts (Comparative Catalysts B and D) and the technique for measuring the properties of these catalysts.

Part A: Preparation of stock silver oxalate/ethylene-diamine solution for use in catalyst preparation:

1) Dissolve 415 grams (g) of reagent-grade sodium hydroxide in 2340 millilitres (ml) deionized water.

Adjust the temperature to 50 °C.

- 22 -

- 2) Dissolve 1699 g of (high purity) silver nitrate in 2100 ml deionized water. Adjust the temperature to 50 °C.
- 3) Add sodium hydroxide solution slowly to silver nitrate solution with stirring while maintaining a temperature of 50 °C. Stir for 15 minutes after addition is complete, and then lower the temperature to 40 °C.
- 4) Insert clean filter wands and withdraw as much water as possible from the precipitate created in step (3) in order to remove sodium and nitrate ions. Measure the conductivity of the water removed and add back as much fresh deionized water as was removed by the filter wands. Stir for 15 minutes at 40 °C. Repeat this process until the conductivity of the water removed is less than 90 µmho/cm. Then add back 1500 ml deionized water.
- 5) Add 630 g of high-purity oxalic acid dihydrate in approximately 100 g increments. Keep the temperature at 40 °C and stir to mix thoroughly. Add the last portion of oxalic acid dihydrate slowly and monitor pH to ensure that pH does not drop below 7.8.
- 6) Remove as much water from the mixture as possible using clean filter wands in order to form a highly concentrated silver-containing slurry. Cool the silver oxalate slurry to 30 °C.
- 7) Add 699 g of 92 percent weight (%w) ethylenediamine (8% deionized water). Do not allow the temperature to exceed 30 °C during addition.

The above procedure yields a solution containing approximately 27-33 %w silver which provides the "stock solution" used in the preparation of Catalysts A and C and Comparative Catalysts B and D below.

#### Part B: Preparation of impregnation solutions

##### For Catalyst A:

To 201 grams of silver stock solution with a specific gravity of 1.562 was added 0.0386 grams of  $\text{NH}_4\text{F}$  in 2 cc

- 23 -

of water. CsOH (50% solution in water) in an amount of 0.1346 grams was added to 50 grams of the above silver solution and the resulting mixture was used for the carrier impregnation.

5 For Comparative Catalyst B:

To 153 grams of silver stock solution with a specific gravity of 1.443 was added 0.0290 grams of  $\text{NH}_4\text{F}$  in 2 cc of water. CsOH (50% solution in water) in an amount of 0.1101 grams was added to 50 grams of the above silver solution and the resulting mixture was used for the carrier impregnation.

10 For Catalyst C:

To 108 grams of silver stock solution with a specific gravity of 1.542 was diluted with 10.7 grams of water. CsOH (50% solution in water) in an amount of 0.0422 grams was added to 36 grams of the above silver solution and the resulting mixture was used for the carrier impregnation.

15 For Comparative Catalyst D:

To 108 grams of silver stock solution with a specific gravity of 1.554 was diluted with 12.1 grams of water. CsOH (50% solution in water) in an amount of 0.0352 grams was added to 36 grams of the above silver solution and the resulting mixture was used for the carrier impregnation.

20 Part C: Catalyst impregnation and curing  
Catalyst A:

Approximately 30 g of carrier A (described above in Table 1) is placed under 25 mm vacuum for 3 minutes at room temperature. Approximately 50 to 60 g of doped impregnating solution (as described in Part B above under "For Catalyst A") is then introduced to submerge the carrier, and the vacuum is maintained at 25 mm for an additional 3 minutes. At the end of this time, the vacuum is released, and excess impregnating solution is

- 24 -

removed from the carrier by centrifugation for 2 minutes at 500 rpm. If the impregnating solution is prepared without monoethanolamine, then the impregnated carrier is then cured by being continuously shaken in a  
5 8500 litre/hr air stream flowing across a cross-sectional area of approximately 3-5 square inches at 240-270 °C for 3-6 minutes. If significant monoethanolamine is present in the impregnating solution, then the impregnated carrier is cured by being continuously shaken in a  
10 8500 litre/hr air stream at 250 °C to 270 °C for 4-8 minutes. The cured catalyst is then ready for testing.

The properties of Catalyst A are shown in Table 3 below.

15 Comparative Catalyst B:

Comparative Catalyst B was prepared in the same manner as Catalyst A, except that Catalyst carrier B was used in place of Catalyst carrier A and the impregnating solution used was that described In Part B above under  
20 "For Comparative Catalyst B". The properties of Comparative Catalyst B are shown in Table 3 below.  
Catalyst C:

Catalyst C was prepared in the same manner as Catalyst A, except that Catalyst carrier C was used in  
25 place of Catalyst carrier A and the impregnating solution used was that described In Part B above under "For Catalyst C". The properties of Catalyst C are shown in Table 3 below.

Comparative Catalyst D:

30 Comparative Catalyst D was prepared in the same manner as Catalyst A, except that Catalyst carrier D was used in place of Catalyst carrier A and the impregnating solution used was that described In Part B above under "For Comparative Catalyst D". The properties of  
35 Comparative Catalyst D are shown in Table 3 below.

- 25 -

TABLE 3  
CATALYST PROPERTIES

	Catalyst A	Comparative Catalyst B	Catalyst C	Comparative Catalyst D
Ag (wt%)	14.5	14.5	14.5	14.5
Cs (ppm)	680	560	300	250

5 The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. The actual level of cesium on the catalyst can be determined by employing a stock cesium hydroxide solution, which has been labelled with a radioactive isotope of cesium, in catalyst preparation. The cesium content of the catalyst can then be determined by measuring the radioactivity of the catalyst. Alternatively, the cesium content of the catalyst can be
 10 determined by leaching the catalyst with boiling deionized water. In this extraction process cesium, as well as other alkali metals, is measured by extraction from the catalyst by boiling 10 grams of whole catalyst in 20 millilitres of water for 5 minutes, repeating the
 15 above two more times, combining the above extractions and determining the amount of alkali metal present by comparison to standard solutions of reference alkali metals using atomic absorption spectroscopy (using Varian Techtron Model 1200 or equivalent). It should be noted
 20 that the cesium content of the catalyst as determined by the water leaching technique may be lower than the cesium content of the catalyst as determined by the radiotracer technique.

25 Part D: Standard Microreactor Catalyst Test  
Conditions/Procedure

- 26 -

1 to 3 Grams of crushed catalyst (0.841-0.595 mm, i.e. 20-30 mesh) are loaded into a 6.35 mm diameter stainless steel U-shaped tube. The U tube is immersed in a molten metal bath (heat medium) and the ends are connected to a gas flow system. The weight of the catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 6800. The outlet gas pressure is 2240 kPa.

The gas mixture passed through the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 25% ethylene, 7% oxygen, 5% carbon dioxide, 61% nitrogen, and 2.5 to 10 ppmv ethyl chloride as a moderator.

The start-up procedure involved ramping the temperature up to 180 °C over a thirty minute period and then up to 190 °C and then up to 200 °C in successive thirty minute periods. Thereafter, the temperature was ramped up at the rate of 10 °C per hour for the next two hours, followed by a further thirty minutes to reach the operating temperature of 225 °C, and then the temperature was adjusted to provide 1.5% ethylene oxide at the reactor outlet. Catalyst selectivity ( $S_{1.5}$ ) and catalyst activity ( $T_{1.5}$ ) were measured at those conditions.

The moderator level is maintained at 10 ppmv for six and one-half hours and thereafter at 2.5 ppmv. Due to slight differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next.

To allow meaningful comparison of the performance of catalysts tested at different times, the Catalysts A and C, and Comparative Catalysts B and D were tested simultaneously with a standard reference catalyst which was  $S_{1.5} = 81.7\%$  and  $T_{1.5} = 235$  °C.

- 27 -

Catalysts A and C and Comparative Catalysts B and D prepared above were tested using the above procedure and the results are given in Table 4 below.

TABLE 4  
CATALYST PERFORMANCE

	S <sub>1.5</sub> , %	T <sub>1.5</sub> , °C
Catalyst A	83.3	227
Comparative Catalyst B	82.5	235
Catalyst C	82.5	232
Comparative Catalyst D	81.7	235

5 As can be seen in Table 4 above, Catalysts A and C,  
which were prepared using an alumina based carrier in  
which a fired body was impregnated with a source of  
titania, have improved initial activities and  
selectivities over Comparative Catalysts B and D,  
10 respectively, which were prepared using an alumina based  
carrier with no source of titania impregnated thereon.

C L A I M S

1. A catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular for the vapour phase production of ethylene oxide from ethylene and oxygen, comprising a catalytically effective amount of silver, a promoting amount of alkali metal, optionally a promoting amount of rhenium and optionally a rhenium co-promoter, deposited on a carrier which carrier is prepared by a process comprising:
  - a) forming a mixture of ceramic components comprising at least one alumina component, ceramic bond, and a liquid medium;
  - b) shaping the mixture into carrier bodies;
  - c) drying and firing the bodies at a temperature of from 1200 °C to 1500 °C to form porous carrier bodies;
  - d) impregnating the porous carrier bodies with a titania generator in a liquid medium; and then
  - e) calcining the impregnated bodies at a temperature sufficient to remove volatiles and generate titania.
2. The catalyst of claim 1 wherein, in step a), at least 80 percent by weight of the ceramic components is provided by alpha alumina.
3. The catalyst of claim 1 wherein, in step a), the ceramic bond material comprises silica, alumina and an alkali metal and is added to the mixture in an amount in the range of from 1 to 3 percent by weight of the alumina components, expressed as alpha alumina, in the mixture.
4. The catalyst of claim 1, wherein, in step a), the mixture comprises:
  - i) an alpha alumina having a first component with a median particle size of from 2 to 4 micrometer and a

- 29 -

second component with a median particle size of 4 to 8 micrometer;

ii) an optionally seeded, hydrated precursor of alpha alumina in an amount sufficient to provide from 5 to 60 percent by weight, basis the total weight of alpha alumina, in the catalyst carrier product;

iii) from 0 to 40 percent by weight, based on the weight of the alpha alumina, of a burnout material;

iv) from 1 to 3 percent by weight, based on the weight of alumina in the composition, expressed as alpha alumina, of a ceramic bond material comprising silica, alumina and an alkali metal; and

v) water in sufficient quantity to shape the above mixture.

5. The catalyst of claim 4 wherein, in the carrier, the precursor of alpha alumina is seeded with sub-micrometer sized particles of alpha alumina in an amount that is from 0.2 to 5 percent by weight, basis the total alumina weight, measured as alpha alumina, in the catalyst carrier.

6. The catalyst of claim 1 wherein, in step d), the titania generator is selected from the group consisting of a titania sol and a solution of a titanium compound containing ligands which form volatile products.

7. The catalyst of claim 1 wherein, in step d), the titania generator is added by impregnation in a volume amount equal to the pore volume of the carrier and sufficient to provide from 0.05 to 10 percent by weight of titania, basis the weight of the finished carrier.

8. The catalyst of claim 1 wherein, in step e), the impregnated carrier is calcined a temperature between 400 °C and 1400 °C.

9. The catalyst of claim 1 wherein the silver ranges from 1 to 40 percent by weight of the total catalyst and the alkali metal is selected from the group consisting of

- 30 -

potassium, rubidium, cesium, lithium and mixtures thereof and ranges from 10 to 3000 parts per million, expressed as the metal, by weight of the total catalyst.

5 10. The catalyst of claim 1 wherein rhenium co-promoter is selected from the group consisting of sulphur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof.

10 11. Use of a catalyst according to any one of claims 1-10 in a process for the epoxidation of one or more olefins having no allylic hydrogen wherein said olefin is contacted in the vapour phase with an oxygen-containing gas at epoxide forming conditions at a temperature in the range of from 75 °C to 325 °C in the presence of an organic halide.

15 12. Use of a catalyst according to any one of claims 1-10 in a process for the production of ethylene oxide wherein ethylene is contacted in the vapour phase with an oxygen-containing gas at ethylene oxide forming conditions at a temperature in the range of from 180 °C to 330 °C.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/02978

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B01J23/66 C07D301/10 B01J23/68

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 908 343 A (BASHIN MADAN M.) 13 March 1990 see claims 1,2,15	1,2,9, 11,12
P,X	WO 96 23585 A (SHELL) 8 August 1996 see claims 1-16	1-3,10
A	EP 0 145 584 A (PRO-CATALYSE) 19 June 1985	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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# INTERNATIONAL SEARCH REPORT

...formation on patent family members

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